

# Exploiting Poly(dimethylsiloxane)-Modified Tips To Evaluate Frictional Behavior by Friction Force Microscopy

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With the aim of investigating the effect of the surface properties on the friction behavior of self-assembled monolayers, we have modified tipless atomic force microscopy (AFM) cantilevers with a poly(dimethylsiloxane) (PDMS) lens. The friction coefficient using the silicon tip is strongly influenced by the mechanical properties of the substrate monolayer because hard, sharp silicon tips penetrate the surface of organic monolayers. However, the friction coefficient obtained for the PDMS-modified AFM cantilever is mostly due to the surface properties of the monolayer functional end group, rather than the viscoelastic deformation of the monolayer. The use of the PDMS tip was demonstrated as a novel means to investigate the effect of surface properties on the frictional behavior of self-assembled monolayers with various functional groups with less mechanical deformation.

## Introduction

Friction between two surfaces plays an important role in processes such as fluidic self-assembly and microelectromechanical systems (MEMS). Moreover, the patterning of organic monolayers on silicon substrates has emerged as an important modifying agent in MEMS devices.<sup>1–6</sup> The use of friction force microscopy to investigate the frictional properties of organic monolayers is a promising method for establishing a fundamental understanding of lubrication phenomena at the molecular level.<sup>7,8</sup> The effect of surface properties on the frictional properties of organic monolayers is well-documented; however, less well-known are the influences of certain mechanical properties which result in viscoelastic deformation of the organic monolayer chains in nanoscale.

Recently, many research groups have documented the effects of end-group functionality on the frictional properties of monolayers using chemically modified atomic force microscopy (AFM) tips.<sup>9–15</sup> However, the hardness and,

indeed, sharpness of the AFM tips invariably result in the tip penetration of the monolayer when a normal force is applied. Frictional behavior using a large microbead such as glass and silica also results in the penetration of the probe as a result of the hardness of the microbead. Amonton's law used in most references assumes that the true contact area is directly proportional to the normal load.<sup>11–15</sup> Therefore, to increase contact area between the probe and the monolayer surface with a normal load, the probe must penetrate on the monolayer surface. The corresponding frictional force is, therefore, a combination of both the mechanical and the surface properties of the organic monolayers.

The mechanical properties of self-assembled monolayers (SAMs) vary according to the preparation conditions (i.e., reaction temperature, humidity, and substrate roughness).<sup>16–18</sup> In addition, the order–disorder transition temperatures associated with these organic monolayers change in accordance with the SAM functional end group, which in turn influences the mechanical properties.<sup>19</sup> Thus, any variation in the mechanical properties will result in molecular deformation of the organic monolayer chains and a concomitant change in the frictional behavior. However, the effect of viscoelastic deformation in monolayers is often overlooked when it comes to investigating the frictional properties of SAMs with various end functional groups.

In this paper, we describe our efforts to monitor the frictional properties of organic monolayers with less mechanical deformation of the monolayer surface, by fabricating an AFM cantilever with a soft poly(dimethylsiloxane) (PDMS) elastomer probe at its apex. The probe has a soft and larger radius of curvature than conventional AFM silicon tips, which is expected to prevent surface penetration when a normal load is applied.

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## Experimental Section

**Materials and Monolayer Preparation.** Octadecyltrichlorosilane [ $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ ; OTS] and 3-aminopropyltriethoxysilane [ $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ; APS] were used as received. All alkylsilane materials and anhydrous toluene were stored in a desiccator prior to use. P-type Si(100) wafers (Shinetsu) were cleaned in piranha solution (70 vol %  $\text{H}_2\text{SO}_4$  + 30 vol %  $\text{H}_2\text{O}_2$ ) for 30 min at 100 °C, then washed with copious amounts of distilled water, and stored in a vacuum prior to use. Vacuum-dried reaction flasks were charged with anhydrous toluene and cleaned Si wafers under argon. The flasks were then placed in a temperature-controlled bath and allowed to stand for 30 min to ensure thermal equilibrium. OTS's were then added to the flask (10 mM) and left to self-assemble on the wafers at 5 and 50 °C for 2 h (under argon). In addition, APS and OTS are deposited on the wafers at room temperature to investigate the effect of the surface properties on the friction behavior of the SAMs.

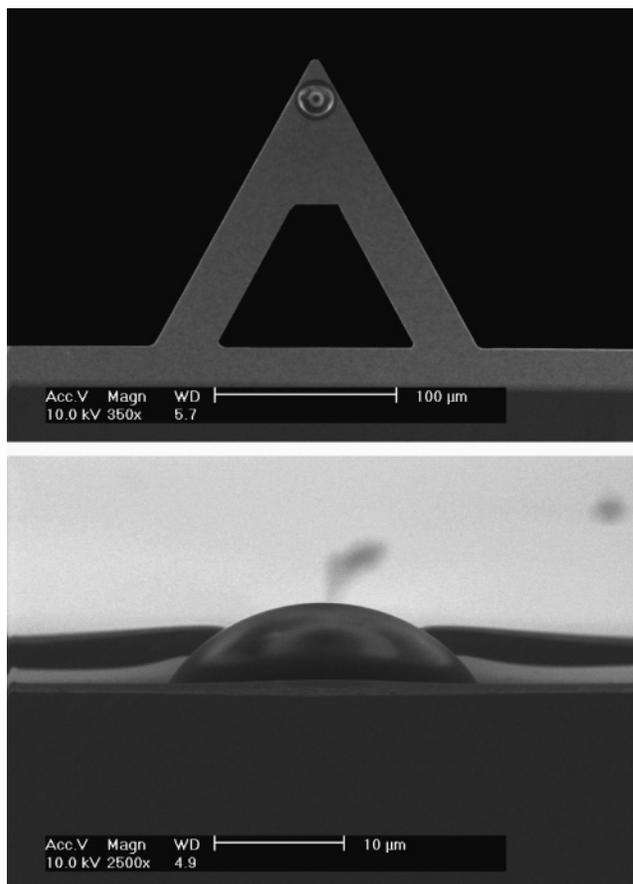
**Monolayer Characterization.** The monolayer thickness was determined using an ellipsometer (M-2000V, J. A. Woollam Co., Inc.). The chain conformation was investigated by analyzing the absorption spectra obtained from a Fourier transform infrared (FT-IR) spectrometer (Bruker IFS 66v), using p-polarized light with an incident angle of 80°. Surface wettability was determined by measuring the contact angle formed between a probe liquid (hexadecane) and the monolayer surface using a contact angle meter (Krüss BSA 10). The monolayer surface topography was examined by AFM (Autoprobe CP, Park Scientific Instruments). AFM images were obtained in contact mode, using silicon nitride cantilevers with a force constant of 0.1 N/m and a scan rate of 1.0 Hz.

**AFM-Tip Modification.** A standard V-shaped, tipless AFM cantilever (Contact Tipless Ultralever B-type, Microscopes) was treated by oxygen plasma for 1 min and then chemically modified with trichloro-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane. The resulting cantilever was placed on a homemade holder and then coated by a PDMS drop (Sylgard 186, Dow Corning) using a sharp needle through optical microscopy. After coating, the PDMS-coated AFM cantilever was cured at 100 °C for 1 h (Young's modulus  $\approx$  1 MPa, Poisson ratio  $\approx$  0.49), yielding a PDMS lens with a radius  $\approx$  14  $\mu\text{m}$ , as determined by scanning electron microscopy (SEM; Figure 1).

**Friction Force Measurements.** Friction measurements were performed using an Autoprobe CP scanning probe microscope (Park Scientific Instruments). Frictional forces were measured by recording traces of cantilever lateral diffraction (friction loops) during 5- $\mu\text{m}$  trace-retrace cycles along a single scan line at 1  $\mu\text{m/s}$ . The resulting friction loops were converted to forces using lateral spring constants.<sup>20,21</sup> All measurements were carried out under a nitrogen atmosphere (relative humidity: 15–20%) to minimize uncertainties arising from capillary forces. These frictional forces were evaluated according to a modification of the Neumeister and Ducker method (silicon tip, 53.3 N/m; PDMS tip, 16.7 N/m),<sup>22,23</sup> taking into account the offset distance of the silicon tip with respect to the end of the cantilever, as measured by high-resolution SEM ( $\approx$ 9  $\mu\text{m}$ ) and the elasticity of PDMS, respectively.

## Results and Discussion

**A. Structure of SAMs.** FT-IR and an ellipsometer were used to determine the structure of OTS monolayers prepared at different temperatures (5 and 50 °C). FT-IR is a powerful tool for the determination of chain orientation. Figure 2a shows the FT-IR spectra of OTS monolayers. The bands at 2919 and 2850  $\text{cm}^{-1}$  are assigned to the asymmetric and symmetric  $\text{CH}_2$  stretching modes, respectively. Characteristic IR peaks resulting from the methylene ( $-\text{CH}_2$ ) stretching vibrations of well-ordered



**Figure 1.** Scanning electron micrograph of a PDMS lens attached to an AFM cantilever.

monolayers (ca. 2919  $\text{cm}^{-1}$ ) were observed for the OTS monolayer deposited at 5 °C. These characteristic peaks exhibit an upward shift for the OTS monolayer deposited at 50 °C, indicating that the ordered, mainly trans-conformation chain structures transform into disordered structures with increasing gauche defects.<sup>24,25</sup> Also, the monolayer thicknesses determined by ellipsometry were about 23 and 15 Å for ordered and disordered monolayers, respectively. This result coincides with the FT-IR observations, implying that a reduction in the monolayer thickness corresponds with an increase in structural disorder and a decrease of the packing density. The structure of monolayers having different chain conformations is schematically represented in Figure 2b.

Figure 2c shows the surface topography of the OTS monolayers and the cross-sectional profile along the line indicated in the image. It can be found that both surfaces are homogeneous and smooth (roughness  $\sim$ 2 Å), irrespective of the monolayer chain conformation. Surface energies for the ordered and disordered monolayers are 21.5 and 22.6  $\text{mJ/m}^2$ , respectively (contact angles of hexadecane: 40 and 36°). The corresponding surface wettabilities for both cases obtained from contact angle measurements were very similar. From these results, we can conclude that the silicon substrates showed complete coverage by OTS monolayers for two cases and that the mechanical properties of the monolayers were not sufficient to alter the surface properties.

**B. Friction Force Measurements.** Friction force versus normal load curves were obtained for the ordered

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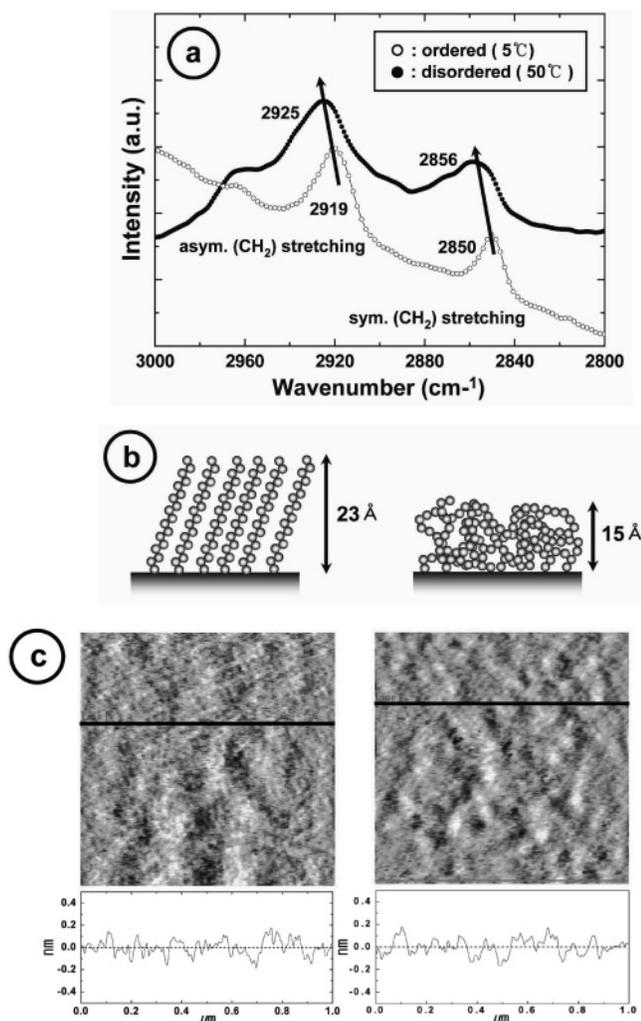
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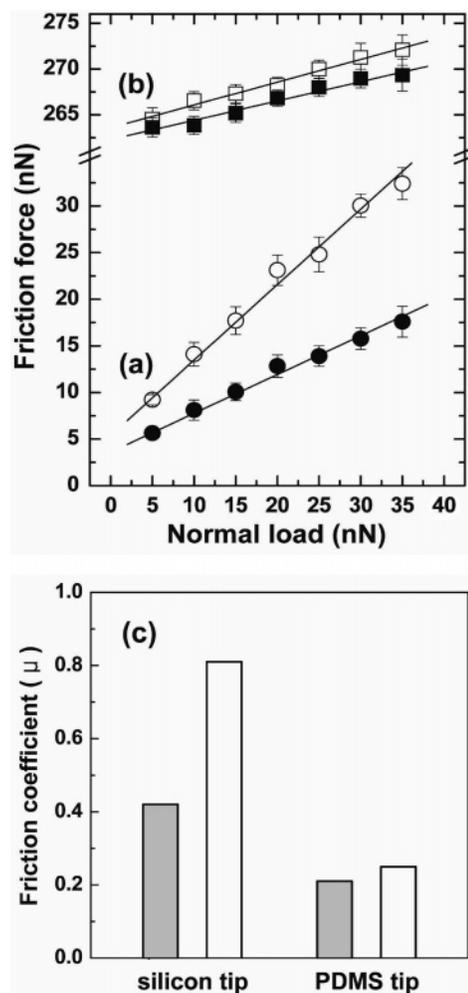


**Figure 2.** (a) Infrared external reflection spectra of the ordered and disordered OTS monolayers on silicon wafers, (b) schematics representing monolayers in both ordered (left) and disordered (right) phases, and (c) AFM images ( $1 \times 1 \mu\text{m}^2$ ) of the ordered (left) and disordered (right) monolayers

and disordered OTS monolayers, measured using a silicon tip and PDMS tip, as shown in Figure 3. Linear regression of the experimental points generates slopes, which demonstrate that the frictional force increases linearly with applied load. These line fits suggest that a modified form of Amontons' law is an appropriate model to describe this frictional behavior. This empirical law holds for macroscopic contacts, where multiple asperity contact statistics are apparent, and the true contact area is assumed to be directly proportional to the normal load.<sup>26,27</sup> In this model, frictional force,  $F_f$ , is related to the applied normal load,  $L$ , as

$$F_f = \mu L + F_0$$

where  $\mu$  is the friction coefficient and  $F_0$  is the residual force which is usually related to the adhesion between the interfacial contacts.<sup>10–11,28</sup> Friction coefficients ( $\mu$ ) are determined from the slopes of the friction force versus load curves. In this system, the residual force for the PDMS



**Figure 3.** Friction force versus applied normal load curves for the ordered (closed) and disordered (open) OTS monolayers on silicon wafers, measured using silicon (a) and PDMS (b) tips. Friction coefficients for the ordered (gray) and disordered (white) OTS monolayers (c).

tip is much greater than for the silicon tip, which is explained on the basis that the PDMS tip has a much larger contact area.

Figure 3a represents the friction force versus normal load curves for the ordered and disordered OTS monolayers using the silicon tip. The friction coefficients ( $\mu$ ) for the two OTS monolayers (ordered and disordered) are 0.42 and 0.81, respectively. The friction coefficient obtained for the disordered OTS monolayer is approximately two times greater than that obtained for the ordered one as shown in Figure 3c. Frictional behavior is attributed to both the surface property and the viscoelastic deformation of the organic monolayers. In the case of the ordered OTS monolayer, the  $\text{CH}_3$  groups are exposed at the surface because of the perfect orientation of the alkyl chains. The surface of the disordered OTS monolayer is presumably composed of  $\text{CH}_2$  and  $\text{CH}_3$  groups. The surface energy of two OTS monolayers is very similar ( $22 \text{ mJ/m}^2$ ). Therefore, the difference of the friction coefficient might be attributed to the viscoelastic deformation of the OTS monolayer during the trace–retrace cycles.

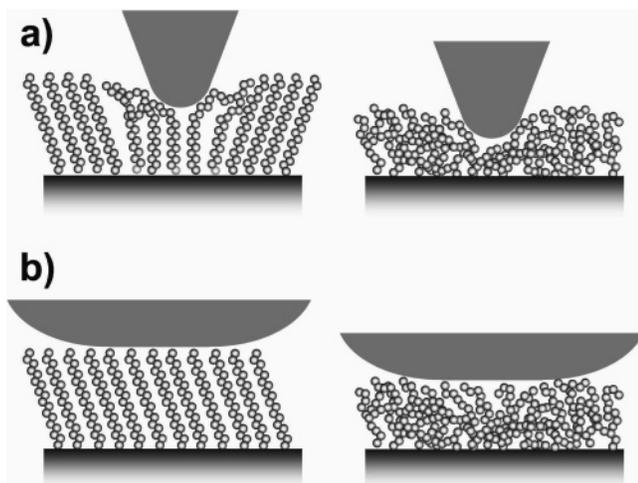
In the case of the ordered OTS monolayer, the penetration depth of the silicon tip may be small because of the rigidity of the monolayer associated with the low chain mobility resulting from the perfect orientation of the monolayer chains. There is small viscoelastic deformation of the monolayer during the trace–retrace cycles, which

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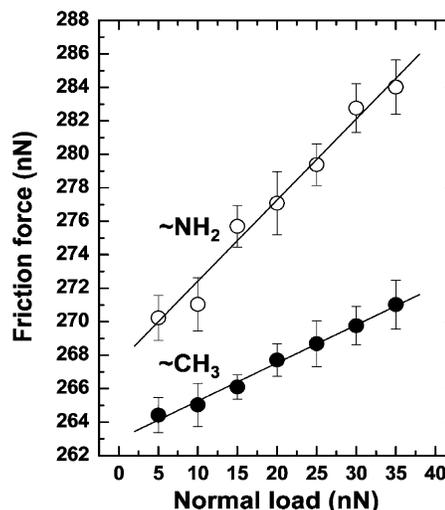
**Scheme 1. Schematic Illustration Depicting the Effects of the Contact Area of AFM Tips on an Organic Monolayer when a Normal Force Is Applied<sup>a</sup>**



<sup>a</sup> (a) Hard, sharp AFM tips penetrate the organic monolayer when a normal force is applied; (b) PDMS tips are not observed to penetrate the surface, because the contact area between the tip and the monolayer increases as a result of PDMS elasticity.

results in a low friction coefficient (0.42). On the other hand, in the case of the disordered OTS monolayer, the monolayer chains are relatively mobile and are deformed more easily. The penetration depth of the silicon tip may be relatively deep. This leads to an increase in the intimate molecular contact at the silicon tip/monolayer interface, which in turn increases the contact area between the tip and the monolayer chains. These include a large amount of viscoelastic deformation during the trace–retrace cycles. Therefore, the friction coefficient (0.81) increases considerably. From these results, we can conclude that the friction coefficient using the silicon tip is strongly influenced by the mechanical properties of the monolayer because hard and sharp silicon tips penetrate the organic monolayers, as shown in Scheme 1a.

The mechanical properties of the organic monolayers vary according to the preparation temperature. In addition, the mechanical properties of the monolayer chains change with change in the end functional group of the SAM even though the SAMs are prepared at the same temperature.<sup>19</sup> Any variation in the mechanical properties will result in viscoelastic deformation of the organic monolayer chains and a concomitant change in the frictional behavior. To identify the contribution of the surface properties to frictional behavior, we have modified the AFM cantilever by attaching a soft PDMS elastomer, which is expected to prevent surface penetration when a normal load is applied. Friction coefficients using the PDMS tip are presented in Figure 3c. The friction coefficients for the ordered and disordered OTS monolayers are almost similar (0.21 and 0.25). The slight increase of the friction coefficients for the disordered OTS monolayer may be attributed to the mobility of the monolayer chains. However, the friction behavior for the PDMS tip is less affected by the change of the mechanical properties in comparison with that of the silicon tip. The PDMS lens is sufficiently elastic such that, when a normal load is applied, the contact area increases as shown in Scheme 1b. Therefore, we can minimize the effect of the mechanical properties of the monolayers on the friction coefficient. The friction coefficient obtained for PDMS tips is mostly



**Figure 4.** Friction force versus applied normal load curves for the APS ( $\text{NH}_2^-$ ) and OTS ( $\text{CH}_3^-$ ) monolayers prepared at room temperature, measured using the PDMS tip.

due to the surface properties of the monolayer functional end group rather than the viscoelastic deformation of the monolayer.

By using the PDMS tips which prevent the surface penetration of the probe, we investigated the frictional behavior of SAMs that have different surface energies [ $41.2 \text{ mJ/m}^2$  (APS) and  $21.5 \text{ mJ/m}^2$  (OTS)]. Figure 4 shows the friction force versus normal load curves for the APS and OTS monolayers prepared at room temperature using the PDMS tip. The friction coefficients ( $\mu$ ) for the APS and OTS monolayers are 0.48 and 0.23, respectively. The use of the PDMS tip can be expected to minimize the effect of the chain conformation and alkyl chain length of the monolayers on the friction coefficient because the contact area increases as shown in Scheme 1b. Therefore, the difference between the frictional coefficients in the two cases is mainly attributed to the difference the between surface properties of the two organic monolayers.

## Summary and Conclusion

Friction behavior of the ordered and disordered monolayers was investigated by using the silicon and PDMS tip to investigate the effect of the penetration of the silicon tip. In the case of the silicon tip, the friction coefficient obtained for the disordered OTS monolayer is approximately two times greater than that obtained for the ordered one. Friction behavior using the silicon tip is strongly influenced by the mechanical properties of the monolayer because hard, sharp silicon tips are known to penetrate the surface of organic monolayers. However, to minimize the effect of the mechanical properties due to the penetration of the silicon tip, the tipless AFM cantilever was modified by a soft PDMS elastomer. The friction coefficient obtained for PDMS tips is mostly due to the surface properties of the monolayer functional end group rather than the viscoelastic deformation of the monolayer.

The use of the PDMS tip was demonstrated as a novel means to investigate the effect of surface properties on the frictional behavior of SAMs with various functional groups with less mechanical deformation.

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**Supporting Information Available:** Evaluation of the lateral spring constant for both the silicon and the PDMS tips (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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